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DEVELOPMENT OF X-RAY FLUORESCENCE SPECTROSCOPY FOR ELEMENTAL ANALYSIS OF PARTICULATE MATTER IN THE ATMOSPHERE AND IN SOURCE EMISSIONS

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Naval Research Laboratory

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ENVIRONMENTAL PROTECTION TECHNOLOGY

Development of X-ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions

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by

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CONTENTS

ABSTRACT 1

INTRODUCTION 2

STANDARDS 4

FILTER MATERIALS 5

EXPERIMENTAL APPROACH 7

Wavelength Dispersion 7

Energy Dispersion 9

RESULTS 10

Sensitivity 11

Detection Limit 13

Analysis of EPA Samples 16

CONCLUSIONS 22

Particle Size Effect 25

Data Handling for Routine Analysis 25

APPENDIX 1 . . . . . A-1-1

APPENDIX 2 . . . . . A-2-1

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ABSTRACT

The application of x-ray fluorescence to the analysis of air pollution particulate samples was demonstrated to be a rapid and economical technique at concentrations encountered in practical situations. No sample preparation is necessary for particulates deposited on filters, which can be placed directly in the x-ray equipment. Because the specimens are thin, matrix absorption and fluorescence are negligible and calibration curves are linear. All of the elements of interest can be measured simultaneously in 100 seconds with either multichannel x-ray crystal spectrometers or multichannel analyzers with energy dispersion detectors.

Sensitivity and detectability were compared for four types of excitation (x-ray tubes, fluorescers, radioisotopes and high-energy ions) and for the two types of data acquisition (crystal spectrometers and energy dispersive detectors). Typical detection limits for 100 seconds measurements varied from 100 to 6000 ng/cm^2 for isotope excitation to 10-250 ng/cm^2 with ordinary laboratory x-ray spectrometers and to 1-5 ng/cm^2 with either large production-type x-ray spectrometers or with high energy ion excitation (ion excitation required special thin substrates and would not be suited to large scale routine use).

The x-ray analysis of real pollution samples showed concentrations for elements of interest between 50 ng/cm^2 and 300 μg/cm^2. Represented among these samples were particulates filtered from auto exhaust, municipal incinerators, a power plant and a cement plant.

For routine analysis of large numbers of samples for many elements the optimum technique requires the use of a multichannel crystal spectrometer instrument capable of measuring a minimum of 12 to 14 elements at the same time. With a minimum degree of automation such instrumentation would be capable of analyzing 600 samples per 24 hour day with a minimum detectable limit for elements above Na in the periodic table in the range of a few to a few hundred nanograms per square centimeter. The addition of an energy dispersion channel using a high resolution semiconductor detector would be desirable for a qualitative confirmation that the crystal spectrometers are measuring the elements of prime concern in the sample.

INTRODUCTION

The elemental analysis of air pollution particulate samples from the ambient air or from emission sources is a rather unique problem. The total amount of material is small, but the sample may contain a large number of elements over a wide atomic-number range and at widely different concentrations. A viable technique must be capable of measuring the elements of interest in an efficient and economical manner. It must have good detectability because of the small amount of some elements present in an air pollution sample.

There are three instrumental analytical techniques other than x-ray fluorescence which are used to varying degrees for the determination of the composition of air pollution particulates; optical emission spectroscopy, atomic absorption spectroscopy and neutron activation. Each of these techniques has sufficient sensitivity for the problem but each also has some specific disadvantages. Arc or spark source optical emission is only semi-quantitative for some elements at best because of difficulty obtaining uniform excitation. The use of microwave or radio-frequency coupled plasmas show some promise but non-equilibrium in the plasma may affect quantitative interpretation. Atomic absorption requires that the sample be in solution and permits the measurement of only one element at a time. As with optical emission, some elements (the non-metals particularly) cannot be analyzed at all by atomic absorption. Neutron activation is perhaps the most sensitive technique for many elements. Among the elements of interest in air pollution particulates, Pb, Fe, and S are three for which neutron activation has poor detection limits. A particular disadvantage of neutron activation for samples containing more than about five elements is the necessity to perform radio-chemical separations or to count several times over extended periods to avoid interferences.

X-ray fluorescence* appears attractive for the analysis of air pollution particulates for several reasons;

1. No specimen preparation is required for filter collections; the material on the filter is analyzed directly.

*For readers unfamiliar with x-ray fluorescence analysis, appendix 1 gives a brief description of the technique.

2. Detectability is fairly uniform across the periodic table and all elements from atomic number 11 (Na) upwards can be analyzed.
3. X-ray technique is non-destructive and samples can be retained for further analysis or as legal evidence.
4. Ten or twenty elements can be analyzed in one time period with presently available commercial equipment for a cost of a few dollars per sample.[1]

X-ray measurements of air pollution particulates have been reported in the literature[2-8] but these have been limited in scope and no systematic comparison has been made of the various excitation and detection methods. The purpose of the work reported here was to examine the various excitation sources and the techniques of measuring the characteristic x-rays so that a realistic comparison might be made.

The objective is to furnish a suitable basis for choosing the most applicable x-ray technique for air pollution problems.

STANDARDS

The importance of proper standards for quantitative analysis cannot be overemphasized. Accuracy of the standard concentrations will determine the limit with which the unknowns can be analyzed. For this reason it is desirable that the concentrations of the standards be determined gravimetrically. Appendix 2 describes the technique used to prepare our calibration standards. We have chosen to express the concentrations in $\mu g/cm^2$ and make the analytical determination on a per-unit-area basis. It is, of course, straightforward to convert to a volume unit, such as $\mu g/m^3$ simply by knowing the area of the sample on the filter and the volume of effluent (or ambient air) sampled.

FILTER MATERIAL

In any technique of micro- or trace-analysis, one of the most important questions concerns the "reagent blank". In x-ray analysis of air pollution particulates on filter substrates the "reagent blank" consists of only the impurities in the filter material. It is obviously desirable that the sample be collected on the purest filter available. Although glass fiber filters have been used extensively because of their strength, the impurity level is very high and varies significantly from batch to batch. Table I lists the concentration of some elements of interest in a typical glass fiber filter and in a membrane filter (Millipore) of considerably higher purity. These data are the results of emission spectrographic analysis and were provided to us by the Environmental Protection Agency (EPA). Also listed in Table I are some neutron activation results (from reference 9) for Millipore and for Whatman filter paper. Whatman filter paper was chosen intuitively as the best substrate on which to prepare our standards and was checked by scanning a limited wavelength range in the crystal spectrometer; it showed no observable peaks. The purity of this substrate was confirmed by the neutron activation analysis. The final three filter materials listed in Table I were tape filters being considered for use in a tape sampler. The requirements for the filter material used in a tape sampler to be strong mitigates against Millipore and other materials must be considered. The three candidate materials listed were analyzed by x-ray fluorescence giving the results shown and indicating high impurity levels.

TABLE I

Impurities in Filter Materials

Concentrations ($\mu g/cm^2$)

Element	Emission Spectroscopy (from EPA)		Neutron Activation (from Ref. 6)		X-Ray Fluorescence* (NRL Results)					
					Pallflex E-60		Pallflex E-70		Acrapor AN800	
	Glass Fiber	Millipore	Millipore	Whatman	A	C	A	C	A	C
Al	120	0.06	0.010	0.012		154				
Si	7000	0.1				474		34		61
S	0.25	0.006				1.0		1.0	490**	13
Cl	1.5	0.0006	1.00	0.1		1.7		1.1		669
K	~ 500	0.006	0.10	0.015	16	12		11		
Ca	250	0.3	0.37	0.14	20	29		30		1.1
V	0.025	0.0001	<0.00005	<0.00003				0.2		0.05
Fe	4	0.03	0.04	0.04		0.9		1.0		0.3
Co		0.00002	0.0001	0.0001						
Ni	<0.08	0.001	<0.02	<0.01		0.2		0.2		0.3
Cu	0.024	0.006	0.06	<0.004		0.3		1.2		0.8
Zn	160	0.002	0.007	<0.025	31	31	30	30		0.2
As	0.08									
Se										
Br			<0.002	0.005						
Cd										
Pb	0.8	0.008						0.6		0.6
Mass Thickness (mg/cm^2)	8	5	5	10	3		3		5	

*For X-Ray Fluorescence: A = 71.5 mCi ^{109}Cd, Si (Li) Detector C = Crystal Spectrometer

**Probably Cl rather than S

EXPERIMENTAL APPROACH

There are several experimental approaches to x-ray fluorescence analysis. They may be categorized according to how the characteristic x-rays are generated or how they are dispersed and detected. In the work under this contract we have used and compared nearly all the known variations which are listed below and shown schematically in Figs. 1, 2, and 3.

Generation

1. Primary x-rays from x-ray tubes (W, Cr, Mo, Rh, targets)
2. Monochromatic x-rays from fluorescers excited by x-ray tubes
3. Radioisotopes (^{109}Cd, ^{55}Fe)
4. Positive ions (protons, alpha particles)

Dispersion and Detection

1. Crystal spectrometers with proportional or scintillation detectors
2. Solid state detectors with energy discrimination of the characteristic x-ray lines

Wavelength Dispersion

Most measurements were made with a laboratory type vacuum crystal spectrometer, Fig. 1, and employed only x-ray tube excitation because the other sources did not give sufficient intensity. Cr, Rh, and W target tubes were used, all operated at 900 watts (45 kV, 20 ma). As shown in the figure, the x-ray tube was aligned so that the primary x-ray beam did not strike the sample holder in an area which can be viewed by the collimator, and therefore the mass which can scatter background into the spectrometer is limited to the sample and its substrate. The sample chamber is evacuated

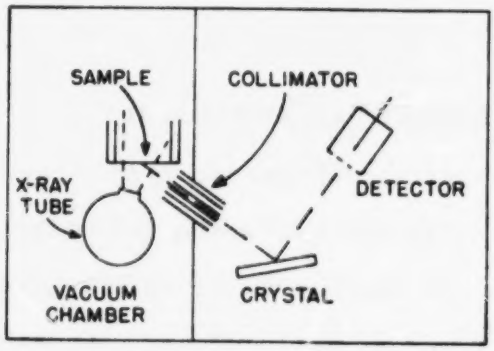

Figure 1. Schematic diagram of the wavelength dispersive crystal spectrometer.

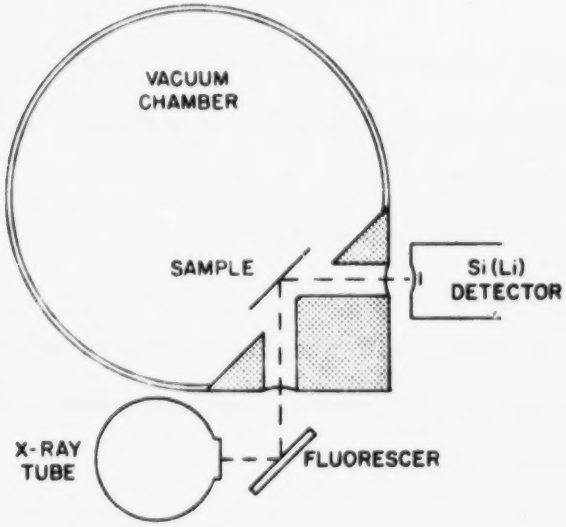

Figure 2. Schematic diagram of the energy dispersion chamber, shown for fluorescer excitation. A radioisotope or an x-ray tube can be placed at the fluorescer position.

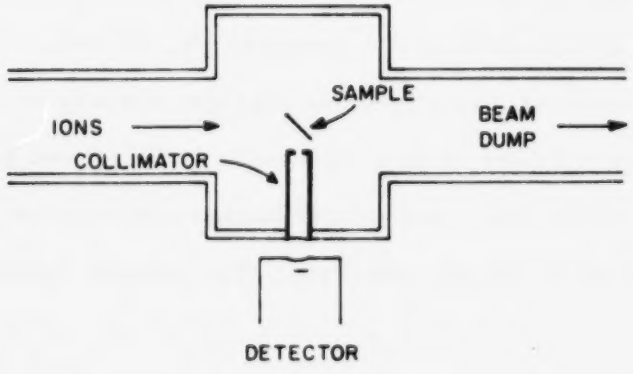

Figure 3. Schematic diagram of the van de Graaff chamber used for ion excitation.

to eliminate air scattering of the primary beam. Fine collimation (0.072° divergence angle) was used to provide good resolution and peak to background ratio. LiF, graphite and KAP (potassium acid phthalate) crystals were used in appropriate wavelength ranges to disperse the radiation. The x-ray lines were measured with a flow proportional counter and pulse height analyzer set for the full width at half maximum of the pulse amplitude distribution.

Energy Dispersion

For the energy dispersion measurements a Si (Li) solid state detector having an energy resolution of about 280 eV at 5.9 keV and 1000 c/s was used. A special vacuum chamber, Fig. 2, was constructed which eliminated air scattering and yet permitted relatively close coupling of the source, sample and detector. The offset geometry was used to prevent the detector from viewing that portion of the chamber wall illuminated by the source. This chamber was used for radioisotope, fluorescer and x-ray tube excitation.

Isotope sources of ^{55}Fe and ^{109}Cd were compared with Mn and Ag fluorescers respectively. The ^{55}Fe isotope was of low activity (~ 7 mCi) and a counting time of 2000 seconds was used to make the ^{55}Fe measurements comparable to the others. A special high activity (~ 70 mCi) ^{109}Cd source was loaned to us by the Atomic Energy Commission (AEC) for the ^{109}Cd measurements. The W x-ray tube exciting the fluorescers was operated at 45 kV (c.p.) and 20 ma. Additional fluorescers of Cu and a composite Cr-Zr powder were also tested.

The x-ray tubes emit so much radiation that, when used for direct excitation, energy dispersion measurements can only be made with the

tube operated at the lowest stable current (3 ma). In addition, a 1/16" pinhole was placed between the x-ray tube and the sample to prevent the intensity from overloading the detector. An x-ray tube capable of stable operation at lower power should achieve the same results.

Ion excitation with 5 MeV protons or alpha particles, Fig. 3, was carried out with the cooperation of the van de Graaff Branch at the Naval Research Laboratory (NRL) and required special standards which could withstand the ion beam current of about 50 nA on 1-2 mm^2. These special standards were prepared by evaporating Cu, Au, or KBr onto thin (10 to 20 $\mu g/cm^2$) carbon or plastic films and calibrating in the x-ray spectrometer by comparison with filter paper standards. The ion beam was collimated so that it struck only the sample and substrate and the detector was shielded from radiation originating at the beam dump. The plastic films showed some Fe and P impurities and the carbon film contained varying amounts of Ti, Si, and Ca plus interference from Fe and occasionally Cu in the sample holder. It is because of the sensitivity of the ion-excitation technique that these low impurity levels are observable.

RESULTS

Results of the measurements made under this contract are divided into two general categories: 1.) Sensitivities and detection limits determined on the filter paper standards, and 2.) Concentrations of the elements in real samples provided by EPA.

The most important goal of the experiments was to compare the various x-ray methods in terms of sensitivity and limit of detectability for the elements

of interest to EPA. By sensitivity we mean the slope of the x-ray intensity versus concentration curve (counts/nanogram per cm^2). Sensitivity depends on excitation-source strength, fluorescent yield, spectrometer and/or detector geometry, and detector efficiency. For detectability we use the definition

$$D.L. = \frac{3\sqrt{B}}{S}$$

where B is the number of counts for the background and S is the sensitivity (the same counting time is used for the B and S measurements).

Sensitivity

The sensitivity was determined for each element of interest from the calibration standards. Three concentrations of each element allowed construction of a calibration curve of x-ray intensity versus concentration. The slope of this curve represents the sensitivity in counts/μg per cm^2. All counting periods, except for the low activity radioisotope source and the ion excitation, were 100 secs. Because of the low counting rate from the ^{55}Fe, counting intervals were 2000 secs. For the ion excitation, the counting period was between 100 and 200 secs, until 5 μC of charge was accumulated.

Table II lists the sensitivities measured by the various x-ray techniques. As expected, sensitivity generally varies smoothly with atomic number except where we change from K to L lines or, for wavelength dispersion, from one crystal to another. For x-ray tubes there is enhanced sensitivity for elements excited by the characteristic radiation from the tube target as can be seen in Table II for the crystal spectrometer measurements of K and Ca

TABLE II

Sensitivities for the Various X-Ray Techniques

$c/\mu g/cm^2$

	Wavelength Dispersion			Energy Dispersion										
	Crystal Spectrometer			Radioisotopes		Fluorescers				X-Ray Tubes			5 MeV Ions	
	100 secs			7 mCi ^{55}Fe	70 mCi ^{109}Cd	100 secs				100 secs			5 μ Coul.	
Element	Cr Tube	Rh Tube	W Tube	2000 s	100 secs	Mn	Cu	Ag	Cr-Zr	Mo	W	W @ Ni foil	Protons	Alphas
Mg	50	112												
Al	78	400												
Si	672	3220												
S	687	3970	290											
Cl	1080	2020												
K	8920	1960											45000	36000
Ca	5620	1430		24	1.8	1210	660	187	700	370	4620	3080		
V	1840	1610	1540	70	3.9	2940	1270	322		1150	8260	4900		
Fe	440	2100	2420		6.0		2200		209	2200	10100	6600		
Co	576	1220	2300											
Ni	422	1230	2000		9.9									
Cu	328	1580	1700										12500	160
Zn	361	1430			14			930	630	3800	6400	6300		
As(Kβ)		78	240											
Se	48	450	600		29			2000	1700	5500	4400	8600		
Br	109	460	400										4300	360
Sr					46			3100		6200		9500		
Zr					54			3300				10600		
Mo					56			3300						
Cd(Lα)	597	840	228											
Pb(Lα)	58	300			15			770						
Au(Lα)													3400	200

with the Cr tube, S and Si with the Rh tube, Fe and Co with the W tube. For energy dispersion measurements there is enhancement of Sr and Se with the Mo tube and again Fe with the W tube. If the characteristic lines are filtered from the x-ray tube spectrum, the sensitivity becomes more or less uniform over a fairly wide atomic number range as is illustrated by the data for the energy dispersion measurements using the W tube with a Ni filter. Radioisotopes and fluorescers are essentially monoenergetic sources; they are efficient in exciting neighboring elements but become less and less efficient for elements of lower atomic number as shown in the Table. The sensitivity for the fluorescers is between 50 and 100 times as high as for the radioisotopes illustrating the effect of the higher intensity available from the fluorescers. Excitation with 5 MeV protons or alpha particles is particularly effective for low atomic numbers but falls off with increasing absorption edge energy; the decline is faster for alpha particles than for protons. An energy of 5 MeV is not high enough energy for efficient excitation of the higher atomic numbers and more energy is required by alphas than by protons for comparable excitation.

Detection Limit

The detection limit might be expected to improve with sensitivity and, to a first order approximation, this is true. However, the additional dependence of the detection limit on the background intensity makes the detectability fluctuate somewhat. The background varies from element to element depending on the impurity level in the substrate, the magnitude of the primary radiation scattered by the sample and stray radiation originating as scattering or fluorescence from various parts of the equipment.

Table III lists the 100 sec. detection limits as measured; it must be emphasized that these are single element detection limits determined on standards containing no interfering elements. However, the background fluctuations due to the impurity level in the substrate (quite low for the Whatman filter paper used to prepare the standards), the scattered primary radiation and the fluorescence from the equipment are reflected in the results because these are unavoidable. If the background is increased due to other elements present in the sample, the detection limit will degrade by the square root of the increase in this background. Since the magnitude of the interference is a function of the resolution (which defines line overlap), the problem is more serious for energy dispersion than for wavelength dispersion. The Si (Li) detector used for the energy dispersion measurements shown in Table III had a resolution of ~ 280 eV which is about a factor of two poorer than the best detector available now. If a state-of-the-art detector was used, the values reported in the table would have been better by about the square root of two. An improvement of another factor of two might be realized with such a detector because of increased counting rate capability compared to the detector actually used. With a higher powered x-ray tube such as presently available, the crystal spectrometer measurements could have detection limits better than listed by a factor of about two also. Of the measurements made by energy dispersion using x-ray excitation, only those using x-ray tubes directly are comparable over a reasonable atomic number range with the wavelength dispersion results.

The ion excitation results show quite good detection limits over a wide atomic number range (especially for protons) even though the sensitivity

TABLE III

Detection Limits for the Various X-Ray Techniques

$\mu g/cm^2$ (corrected for F.P. Absorption)

	Wavelength Dispersion			Energy Dispersion									
	Crystal Spectrometer			Radioisotopes		Fluorescers				X-Ray Tubes			5 MeV Ions
	100 secs			7 mCi ^{55}Fe	70 mCi ^{109}Cd	100 secs				100 secs			5 μ Coul.
Element	Cr Tube	Rh Tube	W Tube	2000 secs	100 secs	Mn	Cu	Ag	Cr-Zr	Mo	W	W w Ni foil	Protons	Alphas
Mg	0.45	0.26												
Al	0.36	0.085												
Si	0.049	0.011												
S	0.052	0.013	0.052											
Cl	0.087	0.019												
K	0.003	0.018												
Ca	0.010	0.029		0.11	6.2	0.058	0.062	0.31	0.084	0.35	0.035	0.073	.001	.001
V	0.053	0.033	0.029	0.18	2.1	0.051	0.068	0.36		0.16	0.031	0.049		
Fe	0.15	0.030	0.036		2.2		0.044		0.35	0.12	0.044	0.062		
Co	0.11	0.084	0.035											
Ni	0.18	0.070	0.037		1.1									
Cu	0.16	0.049	0.040											
Zn	0.18	0.051			1.4			0.18	0.21	0.12	0.17	0.056	.002	*
As		0.15	0.10											
Se	0.82	0.15	0.10		0.42			0.069	0.044	0.072	0.12	0.044		
Br	0.39	0.21	0.16										.001	.010
Sr					0.25			0.051		0.064		0.042		
Zr					0.23			0.050				0.048		
Mo					0.22			0.066						
Cd(Lα)	0.76	0.28	0.29											
Pb(Lα)	1.0	0.26			0.70			0.19						
Au(Lα)													.005	.020

*Interference from Sample Holder

decreased significantly as shown in Table II for the heavier elements. The detection limit for 5 MeV protons is a direct result of high sensitivity and the low background characteristic of proton excitation. It must be remembered, however, that these measurements were made on standards prepared on low mass (10-20 $\mu g/cm^2$) nitrocellulose or carbon substrates. The use of standard filter substrates would require lower beam current and therefore longer counting times to achieve similar detectabilities.

Analysis of EPA Samples

The initial samples received from EPA were of three types: 1.) auto exhaust samples from participants in the Clean-Air Car Race: 2.) ambient air samples taken in New York City under three different atmospheric conditions; and 3.) sixteen samples consisting of approximately 100 mg each of water and benzene extracts of auto exhaust samples. Qualitative analysis of these three types of samples showed readily observable Pb, and Br, and Fe in the Car Race samples and in the auto exhaust material, and Pb and Fe in the New York City samples.

The second set of samples consisted of four collections from the Dade County (Florida) incinerator on Millipore filter and one auto exhaust sample on teflon impregnated fiberglass. The results are shown in Table IV. Results are missing for some elements on some samples because of deterioration of the sample during handling.

The third and largest group of specimens analyzed under this contract were obtained from fixed sources sampled by EPA on Millipore filters. A portion of some of the samples was retained by EPA for examination by Atomic Absorption Spectroscopy. Results for all these samples are shown

TABLE IV

Analytical Results on Auto Exhaust Sample
and Dade County Incinerator Samples

Concentration ($\mu g/cm^2$)

	Al	Si	S	Cl*	K	Ca	V	Fe	Co	Ni	Cu	Zn	As	Se	Br	Cd	Pb
Auto Exhaust								1.2									73
Dade County Incinerator																	
#1 5.97 ft^3	0.17	0.09	4.9	19		1.5	ND	0.68	ND	0.06	0.45	14	ND	ND	0.23	ND	15
#2 7.95 ft^3	0.31	0.10	5.6	20		2.6	0.05					20					24
#3 7.50 ft^3								0.63	ND	0.16	0.50	8.7	ND	ND	0.14		13
#4 7.37 ft^3	0.43	0.16	7.2	25		3.1	0.04	0.83	ND	0.07	0.42	11	ND	ND	0.15		16

*Cl may be high in these results due to contamination during handling.

on Table V. Agreement among the various x-ray techniques is fair when one considers that in some cases the samples were not very homogeneously distributed. A case in point might be illustrated by the Cu concentration in Chicago, N.W. Incinerator Sample # 5 which analyzed to be 24 $\mu g/cm^2$ by wavelength dispersion, 3 $\mu g/cm^2$ by energy dispersion and 0.77 $\mu g/cm^2$ by atomic absorption, each measurement on a different portion of the same sample.

The atomic absorption analyses show almost universally low results when compared to the x-ray measurements. This is characteristic of other atomic absorption analyses within our experience. The most likely explanation is that the particulates are highly refractory being the result of high temperature combustion and are therefore difficult if not impossible to dissolve. Since an atomic absorption analysis depends on the sample being in solution, the results almost invariably will be low. X-ray measurements, on the other hand, require no specimen preparation and therefore any errors cannot be ascribed to difficulty in dissolving.

Comparison of the results of these x-ray analyses by energy dispersion with the results by wavelength dispersion points out some of the important facets of the two analytical techniques. The most obvious observation is the fact that the major elements can be measured by either of the techniques using any of the sources (the Chicago Incinerator samples were simply not examined for elements other than Zn and Pb with the ^{109}Cd source). Intermediate concentrations can be analyzed by either energy dispersion or wavelength dispersion providing x-ray tube excitation is used. Elements present at the lowest detectable concentrations can only be measured using

TABLE V Analysis of Fixed Source Samples

CHICAGO N. W. INCINERATOR

Concentration (ug/cm^2)

A = 71.5 mCi ^{109}Cd, Si (Li) Detector
B = W X-Ray Tube, Ni Filter, Si (Li) Detector
C = Crystal Spectrometer
D = EPA Atomic Absorption Analysis

	Sample # 5				Sample # 6				Sample # 7				Sample # 8				Sample # 9			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
Al			.59				2.2				.63				.91					
Si			.62				2.2				.35				.54					
S		22	22			79	56			25	20			55	41					
Cl†		26	81			58	120			38	100			58	100				3.6	
K		18	18			55	40			22	21			51	37				.04	
Ca		4	1.8			16	5.8			3	1.4			12	2.5				.24	
V							.25				.05									
Fe		1	2.4	.97		6	10	6.5		6	2.5	1.4		6	7.2	4.7				.067
Co							.13				.30									
Ni			.25	.15			.66	.24				.15			.24	.38				.12
Cu		3	24	.77		13	7.0	4.9		2	2.5	.66		10	4.4	2.8				.045
Zn	28	33	26	26	205	210	240	229	43	53	58	28	190	220	220	177			0.12	0.22
As				ND*				ND				ND				ND				ND
Se				ND				ND				ND				ND				ND
Br														5	1.3					
Cd				.58			2.2	16			.33	.80			.97	3.7				ND
Pb	32	46	46	11	180	230	280	255	43	56	59	2.1	130	160	180	159				.089

†Cl may be high in the crystal spectrometer data due to contamination during handling.

*ND = not detected in A. A.

Blank = not detected in the XRFA (All elements listed were measured).

Table V (Continued) Analysis of Fixed Source Samples

OTHER INCINERATORS — Concentration ($\mu g/cm^2$)

	73rd St. # 3				73rd St. # 6			SW Bkln # 1				SW Bkln # 3			Tahoe Sludge # 16			Tahoe Sludge # 17		
	A	B	C	D	A	B	C	A	B	C	D	A	B	C	A	B	C	A	B	C
Al																				1.1
Si			.05				.3			.08				1.1			.3			.6
S		27	2.4			17	63		3	3.2		37	9	14		5	8.1		9	20
Cl		19	5.1			14	70		4	17			13	33		2	1.8			5.3
K	7	34	13		48	27	15		2	3.5		13	10	10		2	2.5		5	6.7
Ca	6	6	0.8		15	8	2.0	4	1	.3			3	4.9		1	.4		3	1.5
V														.02						
Fe			1.3	1.4		1.4	2.0	.7	.3	.3	.28	2	3	2.5		.3	.3		1.3	0.8
Co										.04										
Ni		.8	.3	ND		.3	.3		.3	.4	.008			.4		.4	.3		.3	.5
Cu	3	6	4.2	2.4	6	3.4	5.0	1	1	.8	.11	2	2	1.7	1	1	.9	2	1	2.0
Zn	64	60	57	81	148	125	116	9	12	13	11	54	47	37	12	11	13	25	27	32
As				ND							ND									
Se				ND							ND									
Br	3	3	3.3		4	4	3.2	.5		.3		1.4	2	.7	.3	.3	.2	2	2	1.6
Cd				2.0							.097									
Pb	99	98	104	28	100	71	116	4	5	4.4	4.8	30	33	34	10	11	11	28	32	29

Table V (Continued) Analysis of Fixed Source Samples Concentration ($\mu g/cm^2$)

	Union Power Plant						Cement Plant													
	Sample # 12			Sample # 13			1 A-B gas 5.33 ft^3				4 D-B gas 35.75 ft^3			1 A-B oil 28.85 ft^3			1 A-B oil 5.30 ft^3			
	A	B	C	A	B	C	A	B	C	D	A	B	C	A	B	C	A	B	C	D
Al			6.2			2.1														
Si			8.6			2.1			.03				.1			.2			.5	
S		2	21		7	29			.3				.3			.3			.3	
Cl		2							.3				.7			.6			.7	
K		2	2.8			.5			.06			.2	.2			.2			.2	
Ca	6	5	5.6	4	2	3.0			.2		3	1.5	.5	3		.9		2	.8	
V			.07			.06														
Fe	17	20	14	4	3	3.5		.3	.2	.094	.5	.3	.3		.2	.1		.4	.1	.28
Co			.1																	
Ni		.4	.7			.3		.7	.4	.055		.1	.3		.2	.2		.6	.2	.039
Cu		.5	1.1		.3	1.0			.8	.016			1.0		.2	1.0			.6	.031
Zn		.7	.5			.3			.3	.031			.3			.2			.2	.062
As										ND										ND
Se		.4		.4	.3	.7				ND			.2	.1						ND
Br														1.2	1.6	.9	.4	.6	.2	
Cd										ND										ND
Pb		0.1	1.0		.6	.8				.062					.6	.6				ND

wavelength dispersion with a crystal spectrometer. This last observation might seem to be at odds with the comparable single element detection limits demonstrated for the two methods of data acquisition. However, the results illustrate the effect on the detection limit caused by the presence of interfering elements at widely different concentrations. Admittedly, the data reduction scheme used in analyzing these results did not involve computer stripping of the spectra which might have succeeded in identifying one or more of the missing elements. However, the stripping technique which determines low concentrations from the small difference between two large numbers is only a qualitative analysis and is perhaps suspect even for that purpose when operating near the detection limit.

CONCLUSIONS

On the basis of the results of this investigation, it can be concluded that x-ray fluorescence analysis can measure air pollution particulate samples for the elements of interest to EPA at the concentrations encountered in practical situations. It seems appropriate to make some comments at this point on the various facets of the x-ray technique to provide guidance for its application to specific problems.

Various excitation sources were described in the Sensitivity part of the Results Section. Generally, the use of x-ray tubes (high powered for wavelength dispersion, low powered for energy dispersion) will provide the most uniform excitation over a wide atomic number range. The target of this x-ray tube might be chosen to enhance the sensitivity for a small range of atomic numbers if these were of particular interest. The various

monoenergetic sources such as radioisotopes, fluorescers or transmission target x-ray tubes suffer the disadvantage that the sensitivity falls rapidly as the absorption edge energy of the element of interest decreases away from the energy of the primary photons. For some situations, however, the minimum background present with these monoenergetic sources may recommend them.

Most of the early literature references to x-ray analysis of pollution samples[2, 3, 5, 6, 7] used energy dispersion because the samples contained many elements which would make scanning with a crystal spectrometer prohibitively time consuming. Further examination of the problem points out two difficulties with energy dispersion which are not likely to be overcome in the near future:

1.) The best solid-state detector (150 eV resolution) will not separate the $K\alpha$ line of one element from the $K\beta$ line of the next lower atomic number in the region of the first period transition metal elements. Thus all the elements from sulfur to nickel in the list of elements of interest in the pollution problem will require mathematical unfolding to determine the x-ray intensities. Although unfolding is an acceptable process for intensities of similar magnitude it is not adequate for the range of concentrations present in pollution samples.

2.) The solid-state detectors are limited to about 10^4 counts per second if advantage is to be taken of their best resolution. In the energy dispersive mode of operation the detector receives all the radiation at the same time, including the characteristic lines of all the elements of the sample as well as the scattered primary radiation (which may contribute 50% or more of the total). For those elements present at low

concentration in the sample, e.g., 10 ppm, 2×10^5 other photons must be processed for each one photon of interest. At counting rates of 10^4/sec the counting time must be long to achieve reasonable statistics.

Based on these two limitations for energy dispersion we would have to conclude that multichannel crystal spectrometers for wavelength dispersion offer the best approach to large scale analysis of all the elements of interest. There are, however, other situations as outlined below which permit other approaches. The three types of situations into which many pollution problems may fall are:

1.) One or a few major elements of interest present in the sample at concentrations where interferences are negligible, for example, Fe, Pb and Br in air near a major highway. Energy dispersive analysis with a low power x-ray tube or high activity isotope would be adequate. If only one element were present at a concentration much above any others and only that one element were to be measured, a simple proportional counter could make the measurement. For more than one element a solid-state detector would be desirable.

2.) One or two elements of interest in the presence of some interferences and at concentrations near the detection limit. The best resolution solid-state detector would be required and it would be necessary to use an efficient monoenergetic source for high sensitivity and low background. Counting times might have to be 10 minutes or longer.

3.) The more typical types of air pollution particulate samples (to which this report has addressed itself primarily) require the analysis of a single element or many elements at widely different concentrations and

in the presence of significant interference from neighboring elements. This analytical effort seems to require crystal spectrometers for best resolution and the ability to separate most of the lines from possible interferences. For routine analysis of such samples the only practical analytical solution is the use of multichannel wavelength spectrometers. It also seems desirable that these multi-spectrometer machines should have an energy dispersive channel built into them for a qualitative examination of samples to insure that the elements for which the spectrometers are set include all those present in appreciable amounts.

Particle Size Effect

The total amount of material collected for x-ray analysis (up to a mg/cm^2) does not show the usual inter-element effects encountered in bulk specimens. However, there will be a size effect for particles larger than a few microns. Fig. 4 shows the general particle size curve. For 5 μm particles of metallic Fe and Pb, Si in SiO_2, or Ca in $CaSO_4$, the intensity would be reduced to 60-80 % of its value for the same ng/cm^2 concentration but as smaller particles. With size-fractionated samples there is no difficulty in correcting for particle size, but in general, accuracy would be reduced if the bulk of the particles were of large size compared to those in the calibration standard.

Data Handling for Routine Analysis

The simple linear relation between x-ray intensity and concentration for pollution samples means that the x-ray intensity can be converted to concentration electrically with a zero bias to subtract background and an amplifier to adjust for sensitivity. Thus the printout can be ng/cm^2,

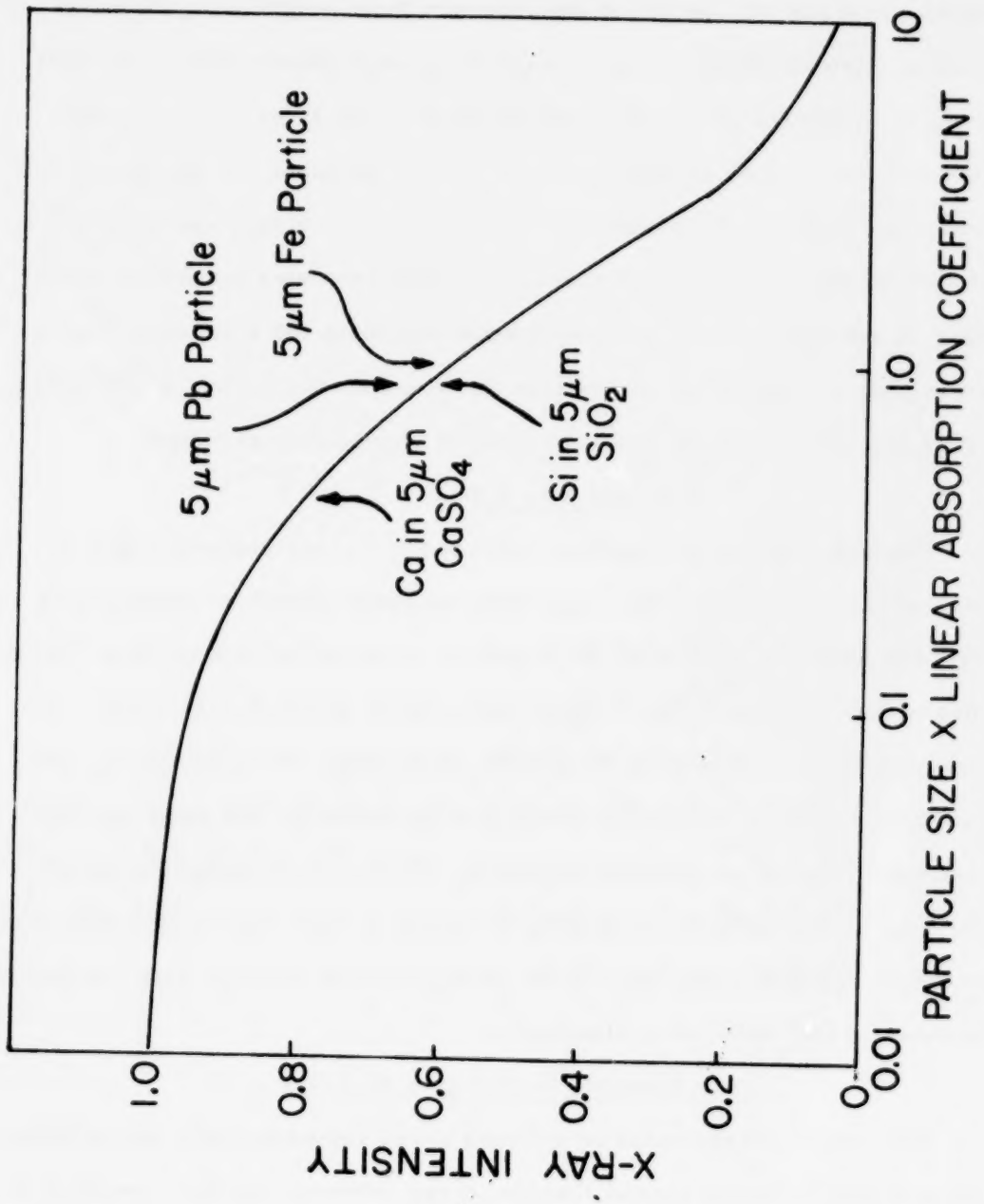

Figure 4. Effect of particle size on x-ray intensity.

$\mu g/cm^2$ or any concentration unit desired without recourse to computers or elaborate data handling equipment. This reduces cost and simplifies operation for untrained personnel.

PHASE II

This report describes Phase I of the development of x-ray fluorescence for elemental analysis of air pollution particulates and a laboratory effort to define the applicability of the x-ray technique to the problem. As was mentioned in the text, the use of x-ray fluorescence as a routine analytical tool requires a multichannel simultaneous x-ray analyzer. The use of separate spectrometers for each element of interest has the unique feature that each channel can be optimized (best crystal, best detector, etc.) for each element. The four major x-ray equipment manufacturers in the free world each produce such an instrument, capable of analyzing between 14 and 24 elements in a single time interval. Phase II of this program is now in progress and involves the evaluation of these commercial instruments for application to routine analysis. The evaluation consists of the determination by NRL personnel of the sensitivity and detection limits for the elements of interest on standards prepared at NRL. These parameters will be compared with those measured during the laboratory phase and some of the real samples analyzed at NRL will be analyzed on the multichannel machines to judge their routine analytical capability.

ACKNOWLEDGEMENT

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APPENDIX I

Fundamentals of X-Ray Fluorescence Analysis

Although the basic principles of x-ray fluorescence are available from a number of texts[A-1 to A-4], it seems appropriate to give a brief description of the technique here for the benefit of those readers of this report who may be unfamiliar with it.

X-ray fluorescence analysis is based on the measurement of the wavelength and intensity of the characteristic x-rays emitted by a sample which has been excited by electrons, photons or ions. A description of the technique can be naturally divided into three areas:

1.) X-Ray Generation

2.) Wavelength and Intensity Measurement

3.) Data Interpretation

A discussion of these three areas will point out the essential details of x-ray fluorescence analysis.

X-Ray Generation

Generation of characteristic x-rays requires two steps: first an atom must be ionized by removing one of its inner electrons; this can be done by bombarding with high energy electrons, ions or photons. Second the missing electron must be replaced by one of the outer electrons. It is the replacement process which causes emission of a characteristic x-ray photon. Figure A-1 which is an energy level diagram illustrates the process schematically and shows the particular transitions for the K and L series lines; for instance if a K-shell vacancy is filled from the outermost L level the $K\alpha_1$ line is emitted.

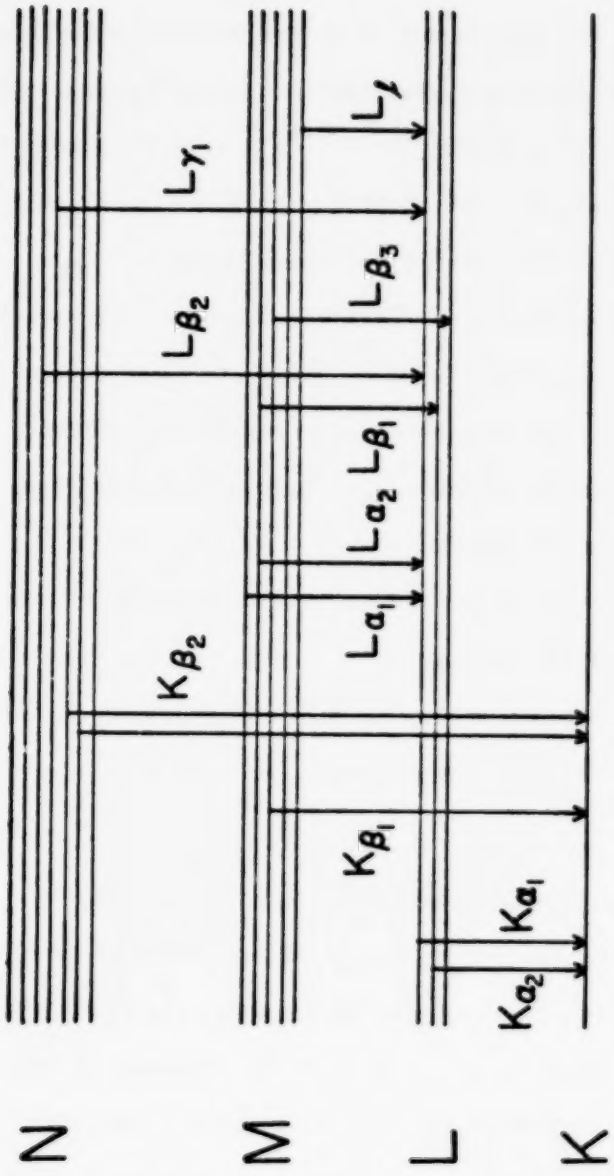

Figure A-1. Schematic energy level diagram of an atom, showing x-ray transitions.

In order to excite the atom the incident quantum must have an energy greater than the binding energy of the inner shell electron being removed. Electrons are the most efficient quanta for generating characteristic x-rays but also generate relatively intense continuous radiation which exists as background under the characteristic line, degrading the detection limit. Electrons are used, of course, in x-ray tubes but are not commonly used in analysis except for the electron probe micro-analyzer where a focused electron beam allows analysis of small local areas in the sample. Ion excitation, such as protons or alpha particles, require the use of a van de Graaff or cyclotron in order to accelerate these particles to high enough energy to produce effective excitation. The heavier particles generate negligible continuum compared to electrons which results in improved detection limits for those samples which lend themselves to high energy ion excitation.

Excitation by x-ray photons is the most common technique in x-ray fluorescence analysis. (Actually a rigid definition of the word "fluorescence" requires that photons be used to generate photons.) X-ray sources used to excite samples include x-ray tubes, x-ray tube-fluorescer combinations and radioisotopes. The most intense of these sources is the x-ray tube; a tungsten target tube operated at the moderate power of 45 kV (c.p.), 20 mA emits about 6×10^{13} ph/s/sr line and continuum radiation. Flourescers are of intermediate intensity; a silver fluorescer excited by a tungsten target tube at 45 kV, 20 mA emits about 3×10^{11} ph/sec/sr of Ag K radiation. On the low end of the intensity scale are radioisotopes; 100 mCi of ^{109}Cd emits about 3×10^{8} ph/sec/sr of Ag K radiation (a higher activity isotope

would, of course, be more intense but would also be hazardous to handle). Photon excitation does not generate any continuum; the primary source of background with x-ray tube excitation is the scattered primary radiation.

Wavelength and Intensity Measurement

The two measurement techniqueswhich are available are wavelength dispersion and energy dispersion, so called because of the means used to identify the characteristic lines of the elements. The wavelength and energy are uniquely related as for all electromagnetic radiation according to the equation

$$E = h\nu$$

where E is the energy, h is Planck's constant and ν is the frequency. The frequency is related to the wavelength (λ) by the velocity of light. When translated into convenient units the equation becomes

$$E = 12398/\lambda$$

with λ in angstroms (Å) and E in electron volts (eV).

The basic principle of wavelength dispersion is the Bragg Equation:

$$n\lambda = 2d \sin \theta$$

where n is the order of diffraction,

λ, as before, is the wavelength,

d is the interplanar spacing of the crystal

and θ is the diffraction angle.

Thus, in an instrument as illustrated by Fig. 1 in the body of this report, the characteristic lines being emitted by the unknown sample can be identified by the θ angle at which they diffract. By selecting suitable crystals it is possible to make measurements over the wavelength range

of about 0.25 to 150 A. The ability to separate two lines of nearly the same energy is called the resolution. For a flat crystal spectrometer, the resolution is a function of the collimator spacing and the rocking curve breadth of the crystal; when combined by the rule of variance, these two parameters define the divergence of the system, $\Delta\theta$, in the differential form of the Bragg Equation:

$$\Delta\lambda = 2d \cos\theta \Delta\theta.$$

Since the resolution is also a function of the θ angle, it will vary over a wide range from about 0.001 to 0.1 Å or from a fraction of an electron volt to several hundred electron volts. The resolution of crystal spectrometers is more than adequate to distinguish each element without interference from either the α or β lines of neighboring elements.

Energy dispersion identifies the elements present in a sample directly by their characteristic photon energies. This is done with an energy sensitive detector which emits a pulse each time an x-ray photon is detected, and the amplitude of this pulse is proportional to the photon energy. (This technique is sometimes called "non-dispersive" to differentiate it from the "dispersive" nature of the analyzing element in a crystal spectrometer.) The detectors commonly used in crystal spectrometers, i.e., gas proportional counters and scintillation counters, have been used in energy dispersion but their energy resolution is poor compared to the solid state, Li drifted, Si detectors presently available. Virtually all of the energy dispersion measurements being made today use the solid state detector, in geometry similar to that shown in Fig. 2 in the body of the report. The energy dispersive system is quite efficient because the detector can accept a large solid angle from the sample,

and therefore make practical use of low intensity sources such as radioisotopes. The resolution of a state-of-the-art solid state detector is about 150 eV at 5.9 keV (Mn Kα), which is poor compared to 14 eV for a LiF crystal spectrometer at the same energy.

In either energy or wavelength dispersion a vacuum path is required if wavelengths longer than about 2.5 Å are to be measured because air absorption becomes significant. Thin detector and source windows are also needed for the work beyond 2.5 Å.

Data Interpretation

Quantitative analysis of pollution samples is far easier than ordinary x-ray fluorescence of bulk material because the amount of sample is too small to show interelement absorption or secondary fluorescence.[A-3] Measured x-ray intensity is converted directly to grams or grams/cm^2 with the individual straight line calibration curves. The only foreseeable difficulty which can occur is with particle size as described in the body of the report.

APPENDIX 2

Preparing Calibration Standards

Sensitivity values and therefore quantitative analysis of unknown samples depends on calibration standards for each of the elements. Two methods of preparing standards were employed: a.) evaporation of 0.25 mℓ of a known solution of a soluble salt of the element onto 9 cm disks of Whatman # 42 filter paper, b.) filtering 11 mℓ from suspension of a known insoluble salt of the element.

Evaporation of Soluble Salts

Table A-1 shows the concentrations prepared for the various elements of interest. Since this method of preparation is a fundamental gravimetric procedure it needs no cross-check except for uniformity of deposit and uncertainty in starting concentration or dilution. Uniformity was measured by cutting 10 one cm squares from the 50 $\mu g/cm^2$ Zn standard and measuring the variation in x-ray intensity. As shown in Table A-2 the standard deviation in the 10 determinations is 4 % relative and the maximum deviation from average is 6 % relative. Variations in preparing stock solution, dilution, and measuring 0.25 mℓ were checked by 6 separate preparations which differed by less than 3 % for any element.

The evaporation method seemed ideal for most elements above atomic number 26 (Fe) because their characteristic radiation would not be absorbed by emergence through the filter paper. For the K lines of elements below 26 in atomic number and for Cd Lα there is increasing absorption and a correction factor as tabulated in Table A-3 was necessary in order to correct to real unknown particles which are all deposited on the surface of Millipore.

TABLE A-1

Concentrations of Elements of Interest in a Typical Set of Standards

Element	Solution	Concentration of 3 Standards ($\mu g/cm^2$)		
Na	NaCl in H_2O	32	7.8	3.0
Mg	MgO in dil. HNO_3	41	11	4.4
Al	$Al_2(SO_4)_3$ in H_2O	51	12	5.7
Si	Na_2SiO_3 in H_2O	23	5.8	2.1
S	$Al_2(SO_4)_3$ in H_2O	90	22	10
Cl	NaCl in H_2O	49	12	4.6
K	KBr in H_2O	23	6.5	2.4
Ca	$CaNO_3$ in H_2O	27	6.8	2.6
V	V in dil. HNO_3	43	11	4.4
Fe	$FeSO_4$ in H_2O	35	8.8	3.5
Co	$CoCl_2$ in H_2O	34	8.6	3.5
Ni	$NiSO_4$ in H_2O	45	11	4.4
Cu	$CuSO_4$ in H_2O	64	16	6.4
Zn	$ZnCl_2$ in H_2O	40	10	4.0
As	As in dil. HNO_3	22	5.6	2.4
Se	H_2SeO_3 in H_2O	35	8.8	3.5
Br	KBr in H_2O	48	13	4.9
Cd	$CdCl_2$ in H_2O	13	3.3	1.6
Pb	PbO in dil. HNO_3	45	12	4.1

TABLE A-2

Uniformity of Deposition for a Standard on Filter Paper

Sample No. (Each 1 cm^2)		Zn Kα Intensity (c/100 secs/cm^2)
1		8880
2		8850
3		9730
4		9650
5		9910
6		9370
7		9130
8		9340
9		9550
10		9320
	Average	9373
	Std. Dev.	350
	Rel. Std. Dev.	3.7%

TABLE A-3

Calculated Filter Paper Absorption Factors

Element	Correction Factor
Na	51
Mg	31
Al	20
Si	14
S	6.3
Cl	4.5
K	2.8
Ca	2.2
V	1.4
Cd(Lα)	3.5

The correction factor relates the x-ray intensity from a given concentration deposited through the volume of the filter paper to the intensity of the same concentration deposited on the surface of the filter. The values listed in Table A-3 are factors by which the sensitivity (in $c/s/\mu g/cm^2$) determined on the filter paper standards are multiplied before comparison with data taken on the real samples. Each correction factor is believed accurate to $\pm$ 25 % but an independent method of preparing particulate standards was desired and led to the filtering of insoluble salts from suspension.

Filtering Insoluble Salts from Suspension

A weighed amount of an insoluble salt of the chosen element was placed in suspension in 500 mℓ of 3:1 glycerine-water mixture so it could be dispersed uniformly. From this, an aliquot of 11 mℓ was made by dipping a beaker into the agitated suspension. This was diluted with 10 mℓ of water to reduce its viscosity so it could be vacuum filtered onto a Millipore substrate.

Initial tests with Fe were compared with the Fe standards prepared by evaporation; agreement was 60 % which indicated that one could prepare standards in the desired range but with somewhat less than the desired accuracy. Therefore a cross check of concentrations was made by neutron activation for the elements below Fe in atomic number. Results are shown in Table A-4 and show some discrepancies which cannot be explained. For Mg, Al, Ca and V for which NAA results seemed reasonable, the particulate standards were checked against the solution standards using the absorption correction factor described in the preceding paragraph. The results given in Table A-5 indicate that the solution standards can be used within a 10-20 % accuracy which seems acceptable for pollution analysis.

TABLE A-4

Results of Neutron Activation Analysis of the Particulate Standards

(Insoluble Salts Deposited from Suspension on Millipore)

Element	Sample Designation	Nominal Conc. ($\mu g/cm^2$)	NAA Result ($\mu g/cm^2$)
Na	H-2	160	210
	E-2	710	980
Mg	L-2	4.3	14*
	M-2	27	31
	H-1	59	53
Al	L-2	8.1	8.2
	M-2	27	12
	H-1	62	37
Si	L-2	7.5	144*
	M-2	25	155*
	H-2	57	190*
S	L-1	3.7	4.7
	H-2	12	15
	M-1	33	43
Cl	H-2	230	475
	E-2	1035	2285
Ca	L-2	5.3	N.D.**
	M-2	18	N.D.
	H-2	40	35
V	L-2	3.9	3.0
	M-2	27	16
	H-2	55	27
Cd	L-1	10	16
	M-2	34	52
	H-1	78	150

*Results considered unacceptable.

**N.D. - Not Detectable

TABLE A-5

Comparison of Solution Standards
After Correction for Filter Paper Absorption
With Particulate Standards for Determining
Sensitivities for Light Elements

Sensitivity ($c/s/\mu g/cm^2$)

Element	Insoluble Salts Deposited on Millipore	Soluble Salts on Filter Paper (Corrected for Absorption in Filter Paper)
Mg	0.50	0.45
Al	1.2	1.6
Ca	14	16
V	16	18

It would be desirable to pursue the preparation of particulate standards further but it was not possible to do this within the present contract.

APPENDIX REFERENCES

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